Tetrahedron 70 (2014) 3123–3133

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Efficient access to fluorinated homoallylic alcohols through an indium promoted fluoroallylation reaction

Gérald Lemonnier, Nathalie Van Hijfte, Muriel Sebban, Thomas Poisson *, Samuel Couve-Bonnaire, Xavier Pannecoucke *

Normandie Univ, COBRA, UMR 6014 et FR 3038, Univ. Rouen, INSA Rouen, CNRS, 1 rue Tesnière, 76821 Mont Saint-Aignan Cedex, France

ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form 15 March 2014
Accepted 19 March 2014
Available online 25 March 2014

Keywords:
Fluorine
Fluoroolefins
Allylation reaction
Indium

ABSTRACT

Herein, an efficient access to fluorinated homoallylic alcohol is reported. The fluorinated alcohols were obtained in good to excellent yield using indium and halo-fluorinated allylic derivatives. The developed methodology using γ-substituted halo-fluorinated allylic derivatives gave the corresponding α-substituted fluorinated homoallylic alcohol in good yields and good diastereoselectivities up to 86:14.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Fluorine atom has the impressive ability to affect the physical and chemical properties of organic molecules.[1] As a result, this intriguing atom is present in around 20% of pharmaceuticals and 40% of agrochemicals.[2] Therefore, it is not surprising that a lot of attention has been recently devoted to the synthesis of fluorinated molecules.[3] Among all the fluorinated molecules, fluoroolefins are of great interest[4] and can be used for instance as peptidomimetics[5] or in material science[6] in order to modify the physical properties. Moreover, fluoroolefins are present in several bioactive compounds, such as anti-diabetics[7] or anti-HIV[8] agents (Fig. 1).

Besides homoallylic alcohols are considered as a key building block in organic synthesis allowing a huge number of post-functionalizations.[9] Thus, as part of our research program devoted to the synthesis of relevant fluorinated building blocks[10] we sought to design a new and straightforward access to secondary and tertiary fluorinated homoallylic alcohols. Although, pioneering work from Allmendinger[11] showed the versatility of such compounds, quite surprisingly the reports dealing with the direct access to these scaffolds are quite scarce in the literature. So far, the synthesis of such compounds remains challenging and to our knowledge, either an Ir-catalyzed dehydrogenative C–C forming bond[12] or a *syn*-selective Hosomi–Sakurai[13] reaction have been successfully reported to access to these compounds (Fig. 2a).

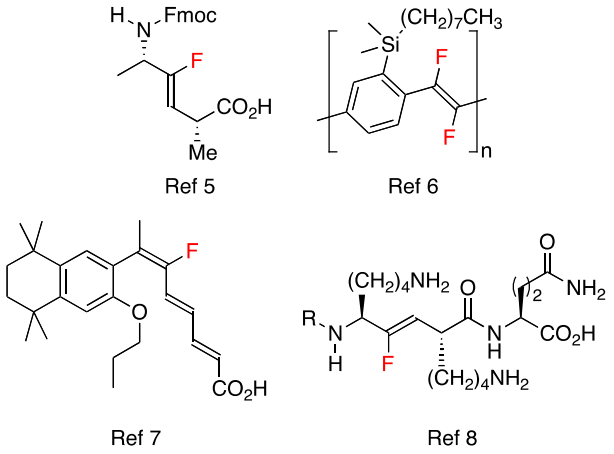


Fig. 1. Examples of relevant fluoroolefins.

Noteworthy, both methodologies required either the use of an expensive noble metal (Ir) or a painstaking synthesis of the fluorinated starting materials. To tackle these major drawbacks, we focused our approach on the use of readily available fluorinated starting material and indium metal as promoter of the allylation

* Corresponding authors. Tel.: +33 2 35 52 24 11; fax: +33 2 35 52 29 59 (T.P.); tel.: +33 2 35 52 24 20; fax: +33 2 35 52 29 59 (X.P.); e-mail addresses: thomas.poisson@insa-rouen.fr (T. Poisson), xavier.pannecoucke@insa-rouen.fr (X. Pannecoucke).

0040-4020/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2014.03.067

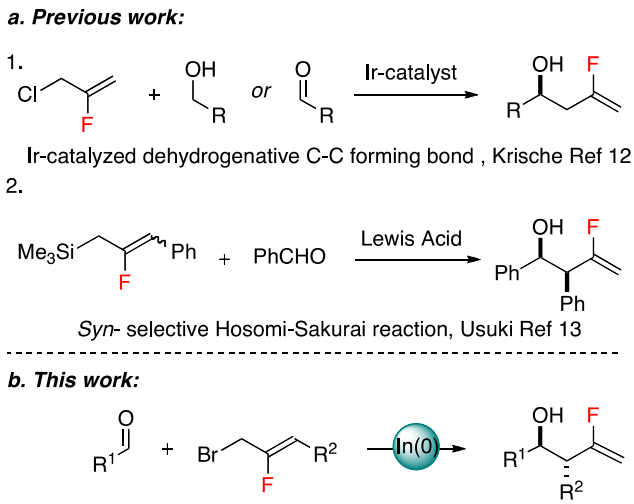


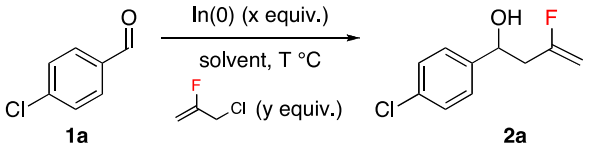
Fig. 2. Access to fluorinated homoallylic alcohols.

reaction (Fig. 2b).[14] Indium metal gives numerous advantages compared to other metal, (1) its use does not require any prior-to-use activation of the metal, (2) indium mediated addition can be used under Barbier conditions, thus avoiding any initial formation of the organometallic species, (3) indium metal and organo-indium derivatives have a broad functional group tolerance and (4) finally indium and associated reagents present a very low toxicity. Thus, we report herein a full account[15] of our investigations to develop an easy access to homoallylic alcohols by means of an indium promoted allylation reaction on carbonyl compounds.

2. Results and discussion

Initially, we focused our attention to the allylation reaction of aldehydes using indium metal and 3-chloro-2-fluoroprop-1-ene as a commercially available fluorinated building block. Our initial attempt using 1.2 equiv of indium metal and 1.1 equiv of 3-chloro-2-fluoroprop-1-ene afforded the desired homoallylic alcohol in 72% yield using water as a solvent (Table 1, entry 1). The use of 2 equiv of indium afforded a slight improve of the reaction yield to 76% (entry 2), while the use of 1.5 equiv of indium and 1.5 equiv of 3-chloro-2-fluoroprop-1-ene gave a significant enhancement of the reaction yield to 90% yield. The use of 2 equiv of indium instead of 1.5 equiv of fluorinated substrate did not provide further improvements (entry 4). Finally, the use of 2 equiv of indium and 3-chloro-2-fluoroprop-1-ene gave the desired product in 91% isolated yield

Table 1
Optimization of the reaction conditions



Entry	Solvent	*x* equiv	*y* equiv	Yield %[a]
1	H_2O	1.2	1.1	72
2	H_2O	2	1.1	76
3	H_2O	1.5	1.5	90
4	H_2O	2	1.5	89
5	H_2O	2	2	98 (91)[b]
6	Brine	2	2	100 (99)[b]

[a] Determined by ^{19}F NMR and ^{1}H NMR of the crude product using an internal standard.
[b] Isolated yield.

(entry 5). Finally, the change of water to brine[16] afforded a complete conversion of the starting material and the product was isolated in nearly quantitative yield (entry 6).

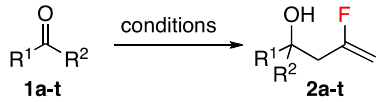
With these established conditions in hand, we moved on the extension of the scope of the reaction (Table 2). First, aromatic aldehydes were engaged under our reaction conditions. Pleasingly, the reaction proceeded smoothly in the presence of electron-withdrawing or electron-donating groups onto aromatic backbones (entries 1–4). Ester derivative **1b** as well as unprotected phenol **1e** are suitable and the desired products **2b** and **2e** were obtained in 88% and 73% yield, respectively (entries 2 and 5). α-Substituted-α,β-unsaturated aldehydes are compatibles and the addition product **2f** was isolated in 87% yield. Next, heteroaromatic compounds were screened and gratefully thiophene adduct **2g** and pyridine derivative **2h** were isolated in good yields (entries 7 and 8). The valuable pyrimidine derivative **1i** bearing a free amine group reacted smoothly, thus affording the product **2i** in 99% yield (entry 9). Ferrocene derivative **1j** gave the addition product **2j** in excellent yield (entry 10). Then, we turn our attention to aliphatic aldehydes, hydrocinnamaldehyde **1k** afforded the corresponding adduct **2k** in 99% yield (entry 11), while nonanal **1l** and citronellal **1m** gave lower yield, 60 and 57% yield, respectively, probably due to their high volatility (entries 12–13). When reactions were carried out with citronellal **1m** and aldehyde **1n** no significant diastereoselectivities were measured (entries 13 and 14). Similarly, (−)-Menthyl glyoxalate hydrate **1o** gave the addition product **2o** in 92% yield as a 1:1 mixture of diastereomers (entry 15). To our delight, this methodology was applied to complexes fluorinated cyclopropanes **1p** and **1q** and the corresponding addition products **2p** and **2q** were obtained in pretty good yield and good to excellent diastereoisomeric ratio (entry 16 and 17).[17] Then, ketones were investigated. Unfortunately, using our standard conditions ketones **1r** reacted poorly and **2r** was obtained in 13% yield along with the recovery of the unreacted starting material (entry 18). Using activated ketone **1s** as starting material, a solvent survey shown that an increase of the temperature to 60 °C using THF as a solvent allowed the formation of the addition product **2s** in 99% yield (entry 19). With these new conditions, ketones **1t** gave the desired adduct in 57% yield (entries 20). Unfortunately, despite several attempts we have not been able to improve the reaction using **1r** as a substrate.

Having established a practical and efficient access to fluorinated homoallylic alcohol, we decided to go further and to design an access to more complex fluorinated structures using elaborated halo-fluorinated allylic compounds. The γ-substituted bromofluorinated allylic derivatives **5** were readily synthesized starting from the corresponding α-fluoroacrylates **3**.[18] Reduction of the ester function mediated by $LiBH_4$ gave the allylic alcohols **4** in pretty decent yields. Then, a bromination reaction of the allylic alcohol **4** using PBr_3 afforded the corresponding γ-substituted bromofluorinated allylic derivatives **5** in pretty good overall yield (Table 3).

With these substrates in hand and in order to settle the optimized reaction conditions we carried out the addition reaction using the bromo derivatives **5a** with 4-chlorobenzaldehyde **1a** under various conditions (Table 4).

First, we checked the influence of the metal on the stereochemical outcome of the reaction and we observed that indium was the best metal to promote the reaction. Indeed, Mn gave no reaction (Table 4, entry 1) while inactivated zinc and tin led to low yield and low diastereoselectivity (entries 2 and 3). We were pleased to observed that indium afforded exclusively the γ-adduct in quantitative yield with a 80:20 *anti*:*syn* diastereoisomeric ratio (entry 4).[19] Next, a solvent survey was performed: THF and DMF gave lower yield and lower diastereoselectivity (entries 5 and 6) while brine affords similar results (entry 7). Interestingly, the reaction proceeded smoothly in EtOH as a solvent. Moreover, we observed

Table 2
Scope of the reaction[a]



1a-t 2a-t

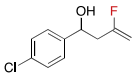
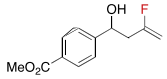
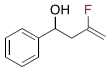
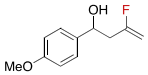
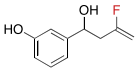
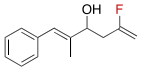
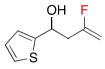
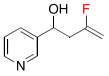
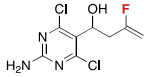
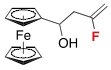
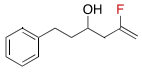
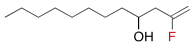
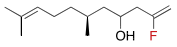
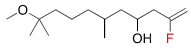
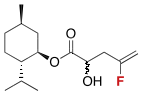
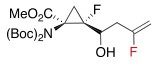
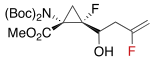
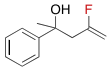
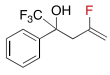
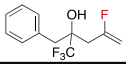
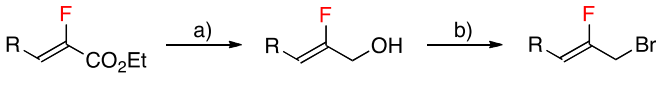
Entry	Starting material	Product		Yield %[b]
1	**1a**		**2a**	99
2	**1b**		**2b**	88
3	**1c**		**2c**	66
4[d]	**1d**		**2d**	99
5	**1e**		**2e**	73
6[c]	**1f**		**2f**	87
7	**1g**		**2g**	83
8[c]	**1h**		**2h**	77
9	**1i**		**2i**	79
10	**1j**		**2j**	99
11[d]	**1k**		**2k**	99
12[e]	**1l**		**2l**	60
13[e]	**1m**		**2m**	57 (53:47)[g]
14[e]	**1n**		**2n**	97 (50:50)[g]
15	**1o**		**2o**	92 (50:50)[g]
16[d]	**1p**		**2p**	63 (80:20)[g]
17[d]	**1q**		**2q**	83 (100:0)[g]
18[d]	**1r**		**2r**	13
19[f]	**1s**		**2s**	99

Table 2 (*continued*)

Entry	Starting material	Product		Yield %[b]
20[f]	**1t**		**2t**	57

[a] Conditions: **1** (1 equiv), 3-chloro-2-fluoropropene (2 equiv), In(0) (2 equiv), brine (0.3 M), rt, 16 h.
[b] Isolated yield.
[c] 72 h reaction time.
[d] Reaction performed at 40 °C for 72 h.
[e] Reaction performed at 60 °C for 24 h.
[f] Reaction performed at 60 °C in THF for 24 h.
[g] Diastereoisomeric ratio determined by ^{19}F NMR on the crude reaction mixture.

Table 3
Preparation of γ-substituted α-bromo fluorinated allylic derivatives **5**



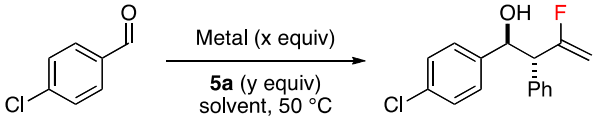
3a-x **4a-x** **5a-x**

a) $LiBH_4$, THF, 0 °C; b) PBr_3, Et_2O, 0 °C.

Entry	R	**4**, %[a]	**5**, %[a]	Overall yield %
1	Ph	**4a**, 94	**5a**, 88	82
2	C_6H_5–$(CH_2)_2$	**4b**, 32	**5b**, 50	16
3	4-Br–C_6H_4	**4c**, 69	**5c**, 91	62
4	4-OCH_3–C_6H_4	**4d**, 92	**5d**, 84	77

[a] Isolated yield.

Table 4
Optimization of the reaction conditions



1a **6a**

Entry	Solvent	Metal	*x* equiv	*y* equiv	Yield %[a] ()[b]
1	H_2O	Mn	1.5	1.5	NR
2	H_2O	Zn	1.5	1.5	33 (64:36)
3	H_2O	Sn	1.5	1.5	48 (ND)
4	H_2O	In	1.5	1.5	95 (80:20)
5	THF	In	1.5	1.5	37 (58:42)
6	DMF	In	1.5	1.5	30 (ND)
7	Brine	In	1.5	1.5	95[c] (79:21)
8	EtOH	In	1.5	1.5	95[c] (82:18)
9	EtOH	In	1	1	90[c] (85:15)
10[d]	EtOH	In	1.5	1.5	100 (83:17)

[a] Determined by ^{19}F NMR and ^{1}H NMR of the crude product using an internal standard.
[b] *anti*:*syn* ratio determined by ^{19}F NMR on the crude reaction mixture.
[c] Isolated yield.
[d] Reaction performed at rt for 24 h.

a cleaner crude reaction mixture than in aqueous media along with a higher *anti*:*syn* ratio. The desired product **6a** was obtained in almost quantitative yield with a 82:18 diastereoisomeric ratio (entry 8). A decrease of the amount of indium metal and **5a** from 1.5 to 1 equiv gave a better diastereoisomeric ratio, 85:15 despite a slight decrease of the reaction yield (entry 9). Finally, we conducted the reaction at room temperature and after 24 h reaction time we have been able to isolate the γ-adducts in nearly quantitative yield with a pleasant 83:17 diastereoisomeric ratio (entry 10).

Noteworthy, only the γ-adduct was observed in the crude reaction mixture and a X-ray analysis of the major product revealed that the process delivered the *anti* adduct as a major diastereoisomer (Fig. 3).[20] Noteworthy, this process represents the

first access to the anti-addition product, whereas Usuki and co-workers[12] approach provides predominantly the *syn*-adduct. Having these conditions in hand we extended the scope of the reaction to various aldehydes (Table 5).

These optimized conditions have been applied to a broad range

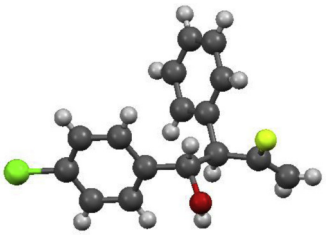


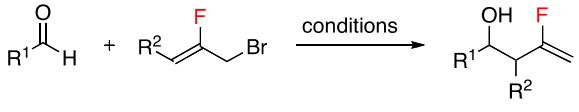
Fig. 3. Relative configuration of *anti*-**6a** by X-ray analysis.

of aldehydes. Reaction was first performed with the bromoallyl derivative **5a**. Electron rich aldehyde **1u** afforded the corresponding additions product **6b** in 87% yield with a pleasant 81:19 diastereoisomeric ratio (entry 2). Piperonal gave the desired product **6c** in 82% yield with a pretty similar diastereoisomeric ratio (80:20, entry 3). Heteroaromatic aldehydes were compatible under our reaction conditions and thiophene adduct **6d** was isolated in 57% yield and a 86:14 *anti*:*syn* ratio (entry 4). To our delight, (*E*)-crotonaldehyde **1w** reacted with **5a** to give the addition product **6e** in good yield with a lower diastereoisomeric ratio (60:40, entry 5). Then reaction was carried out with aliphatic aldehydes, hydrocinnamaldehyde **1k** and pentanal **1x** reacted with **5a** to give the addition product in pretty good yield and a decent *anti*:*syn* ratio, 64:36 and 63:37, respectively (entries 6 and 7). Surprisingly, nonanal gave the corresponding addition product **6h** in a modest yield with 64:36 diastereoisomeric ratio (entry 8). Then, the aliphatic substituted bromo allylic derivative **5b** was tested under our reaction condition. *para*-Chlorobenzaldehyde reacted nicely with **5b** to give the addition product **6i** in 62% yield as an equal mixture of *anti* and *syn* diastereoisomers (entry 9). (*E*)-Crotonaldehyde **1w** was engaged and afforded **6j** in 70% yield with a reverse diastereoselectivity (entry 10), while the aliphatic pentanal gave an equal mixture of *syn* and *anti* diastereoisomers in 50% yield (entry 11). Reaction was then carried out with **5c** and aldehyde **1a** giving the addition product **6l** in 62% yield with a 82:18 diastereoisomeric ratio (entry 12). (*E*)-Crotonaldehyde **1x** and pentanal gave the addition products in good yield with lower selectivities (entries 13 and 14). Finally reaction was carried out with **5d** and **1a** giving **6o** in 37% with a 76:24 diastereoisomeric ratio (entry 15). This modest yield might be easily explained by the low stability of **5d**, due to the presence of the *para*-methoxy substituent.

Finally, in order to define a plausible reaction pathway and transition state the reaction with (*E*)-**5a** was carried out.

Under standard condition, the addition product was isolated in 75% as a 78:22 diastereoisomeric mixture. Interestingly, ^{1}H NMR has revealed that the major diastereoisomer was the anti isomer (Fig. 4). Taking this result into account, we proposed a plausible equilibration of the organo-indium species in favor of the thermodynamically stable Z isomer.[21] This most stable species would react through a six-membered ring transition state. The indium metal center coordinates to the aldehyde and according to a chair like intermediate the addition occurs at the γ-position delivering the anti-product as a major isomer, whatever the geometry of the starting bromofluorinated allylic species (Fig. 5). Noteworthy, the equatorial-equatorial gauche interaction in the favored transition state might explain the observed selectivity. Indeed, better selectivities were obtained in the case of aryl or vinyl substituted

Table 5
Scope of the reaction[a]



1a-y **5a-d** **6a-p**

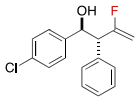
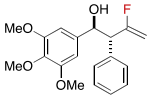
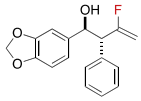
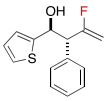
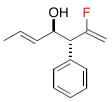
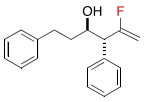
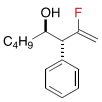
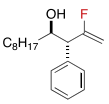
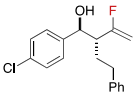
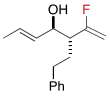
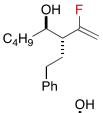
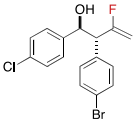
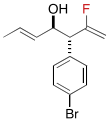
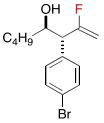
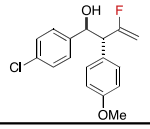
Entry	Starting material	5	Major product		Yield %[b] ()[c]
1	**1a**	**5a**		**6a**	90 (85:15)
2	**1u**	**5a**		**6b**	87 (81:19)
3	**1v**	**5a**		**6c**	82 (80:20)
4	**1g**	**5a**		**6d**	57 (86:14)
5	**1w**	**5a**		**6e**	78 (60:40)
6	**1k**	**5a**		**6f**	83 (64:36)
7	**1x**	**5a**		**6g**	70 (63:37)
8	**1l**	**5a**		**6h**	39 (64:36)
9	**1a**	**5b**		**6i**	40 (50:50)
10	**1w**	**5b**		**6j**	70 (42:58)
11	**1x**	**5b**		**6k**	50 (50:50)
12	**1a**	**5c**		**6l**	62 (82:18)
13	**1w**	**5c**		**6m**	78 (61:39)
14	**1x**	**5c**		**6n**	64 (66:34)

Table 5 (*continued*)

Entry	Starting material	5	Major product	Yield %[b] ()[c]
15	**1a**	**5d**	 **6o**	37 (76:24)

[a] Conditions: **1** (1 equiv), **5** (1 equiv), In(0) (1 equiv), EtOH (0.3 M), 50 °C, 16 h.
[b] Isolated yield of the diastereoisomeric mixture.
[c] *anti*:*syn* ratio determined by ^{19}F NMR on the crude reaction mixture.

substrates, while the use of aliphatic one gave lower selectivities. This difference might be explained thanks to this gauche interaction in the course of the addition through a six members transition state.

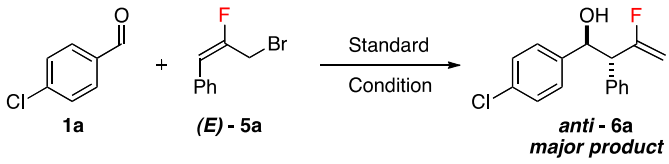


Fig. 4. Reaction with (*E*)-fluorinated olefins.

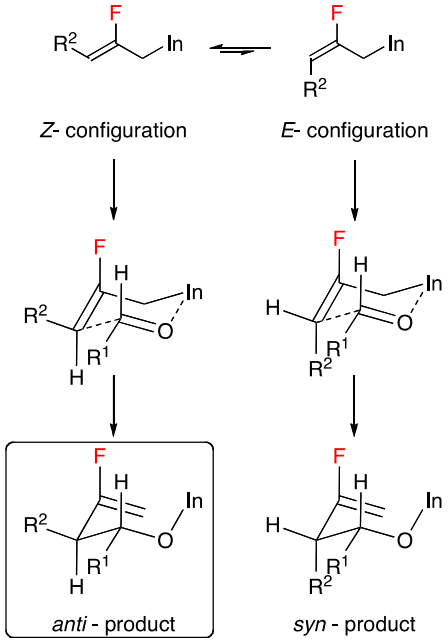


Fig. 5. Proposed transition state.

3. Conclusion

As summary, we developed herein a straightforward access to fluorinated homoallylic alcohol by means of an indium promoted allylation reaction. The synthesis and the use of γ-substituted halofluorinated allylic derivatives afforded the γ-addition products, which have been isolated in good yields and moderate to good diastereoselectivities. An X-ray analysis of the major product revealed that the process furnished predominantly the *anti*-addition product. This methodology represents the first selective access to the anti adducts in good to excellent yields. The reaction scope is quite broad and the process is functional group tolerant. Finally, to explain the stereochemical outcome of the reaction and in agreement with the obtained crystal structure we proposed a six-membered ring transition state.

4. Experimental section

4.1. Materials and instrumentation

All reactions were carried out using an oven-dried glassware using standard Schlenk technique unless otherwise stated. Flash chromatography was performed with silica gel (0.040–0.060 nm). Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator and visualized by UV light (254 nm) and/or chemical staining with $KMnO_4$ solution or PMA solution. ^{1}H NMR spectra were recorded on a Bruker DXP 300, ^{13}C NMR spectra at 75 MHz and ^{19}F NMR spectra at 282 MHz. Chemical shifts (δ) are quoted in parts per million (ppm) relative to residual solvent ($CHCl_3$: δ=7.27 ppm for ^{1}H, δ=77.0 ppm for ^{13}C or relative to external $CFCl_3$: δ=0 ppm for ^{19}F). The following abbreviations have been used: δ (chemical shift), *J* (coupling constant), s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), q (quartet), dq (doublet of quartets), m (multiplet). High-resolution mass spectra (HRMS) were recorded on Waters LCT Premier, IR spectra were recorded on a PerkinElmer Spectrum 100. Melting points are uncorrected.

Fluoroacrylates **3a**–**d** were synthesized according to the literature procedure[18] and 3-chloro-2-fluoroprop-1-ene was purchased from Apollo Chemical. All aldehydes and ketones were recrystallized, distilled or filtered through basic alumina prior-to-use.

4.2. Procedure

4.2.1. General procedure A for the allylation of aldehydes and ketones with 3-chloro-2-fluoroprop-1-ene. In a 1.5 mL vial, indium (23 mg, 0.2 mmol), **1** (0.1 mmol) and solvent (1 mL) were added. Then, 3-chloro-2-fluoroprop-1-ene (18 μL, 0.2 mmol) was added and the vial was sealed (screwed cap). The resulting mixture was stirred at the given temperature for 16 h, DCM was added and the aqueous phase was extracted two times. Organic layer was dried over $MgSO_4$ and the residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate mixture) to afford the corresponding fluorinated alcohol **2** (see Table 2).

*4.2.2. General procedure B for the reduction of fluoroacrylates 3 into homoallylic alcohols **4**.* To a solution of fluoroacrylate **3** (11 mmol) in THF (40 mL) at 0 °C was added $LiBH_4$ (44 mmol) and reaction was stirred at rt for 6 h. The solution was carefully quenched with NH_4Cl (saturated aqueous solution) and extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc mixture) to afford the corresponding fluorinated allylic alcohol **4** (see Table 3).

*4.2.3. General procedure C for the bromination of homoallylic alcohols **4**.* To a solution of alcohol **4** (6.6 mmol) in Et_2O (20 mL) at 0 °C was added PBr_3 (3.3 mmol). The resulting mixture was allowed to reach to rt and stirred for 2 h. The reaction mixture was quenched with $NaHCO_3$ (saturated aqueous solution) and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc mixture) to afford the corresponding fluorinated bromo allylic derivative **5** (see Table 3).

*4.2.4. General procedure D for the allylation of aldehydes with **5**.* In a vial, **5** (0.3 mmol), indium (0.3 mmol), **1** (0.3 mmol) and EtOH (1 mL) were introduced, the vial was sealed (screwed caps) and

heated at 50 °C under vigorous stirring for 16 h. The solution was quenched with five drops NH_4Cl (saturated aqueous solution) and stirred for 10 min. The mixture was filtered throw a pad of Celite (washed with DCM) and concentrated. The residue was purified by flash chromatography (SiO_2, cyclohexane/EtOAc mixture) to afford the corresponding fluorinated alcohol **6** (see Table 5).

4.3. Physical and spectral datas

4.3.1. 1-(4-Chlorophenyl)-3-fluorobut-3-en-1-ol ***2a*** *(Table 2, entry 1).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.27 (m, 4H), 4.98–4.87 (m, 1H), 4.65 (dd, J=17.3, 2.9 Hz, 1H), 4.33 (dd, J=49.9, 2.9 Hz, 1H), 2.69–2.48 (m, 2H), 2.26 (d, J=2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (d, J=257 Hz), 141.6, 133.7, 128.8 (2C), 127.2 (2C), 93.2 (d, J=19 Hz), 70.4, 42.4 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.9 (ddt, J=50, 21, 17 Hz). IR (cm^{-1}): 3375, 1674, 1046, 802. Anal. Calcd for $C_{10}H_{10}ClFO$: C, 59.86; H, 5.02. Found: C, 59.80; H, 5.00.

4.3.2. Methyl 4-(3-fluoro-1-hydroxybut-3-enyl)benzoate ***2b*** *(Table 2, entry 2).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J=8.1 Hz, 2H), 7.43 (d, J=8.3 Hz, 2H), 5.01 (t, J=6.6 Hz, 1H), 4.65 (dd, J=17.2, 2.9 Hz, 1H), 4.33 (dd, J=49.8, 2.8 Hz, 1H), 3.90 (s, 3H), 2.67–2.52 (m, 2H), 2.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 162.7 (d, J=257 Hz), 148.1, 129.9 (2C), 129.6, 125.6 (2C), 93.2 (d, J=19 Hz), 70.4, 52.2 (d, J=3 Hz), 42.3 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.0 (dq, J=50, 18 Hz). IR (cm^{-1}): 3473, 1696, 1671, 1286, 765, 704, 537. Anal. Calcd for $C_{12}H_{13}FO_3$: C, 64.28; H, 5.84. Found: C, 64.64; H, 5.82.

4.3.3. 3-Fluoro-1-phenylbut-3-en-1-ol ***2c*** *(Table 2, entry 3).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.27 (m, 5H), 5.03–4.90 (m, 1H), 4.66 (dd, J=17.3, 2.7 Hz, 1H), 4.35 (dd, J=50.0, 2.5 Hz, 1H), 2.75–2.53 (m, 2H), 2.17 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, J=257 Hz), 143.2, 128.7 (2C), 128.1, 125.8 (2C), 93.0 (d, J=19 Hz), 71.0, 42.4 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.9 (ddt, J=50, 21, 17 Hz). IR (cm^{-1}): 3375, 1674, 852, 756, 698. Anal. Calcd for $C_{10}H_{11}FO$: C, 72.27; H, 6.67. Found: C, 72.25; H, 6.68.

4.3.4. 3-Fluoro-1-(4-methoxyphenyl)but-3-en-1-ol ***2d*** *(Table 2, entry 4).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J=8.5 Hz, 2H), 6.89 (d, J=8.5 Hz, 2H), 4.90 (dd, J=8.3, 5.1 Hz, 1H), 4.63 (dd, J=17.4, 2.7 Hz, 1H), 4.33 (dd, J=50.1, 2.5 Hz, 1H), 3.80 (s, 3H), 2.75–2.45 (m, 2H), 2.20 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, J=257 Hz), 159.3, 135.3, 127.0 (2C), 113.9 (2C), 92.7 (d, J=19 Hz), 70.5, 55.3 (d, J=3 Hz), 42.2 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.7 (dddd, J=50, 22, 17, 15 Hz). IR (cm^{-1}): 2909, 1675, 1511, 1241, 828. Anal. Calcd for $C_{11}H_{13}FO_2$: C, 67.33; H, 6.68. Found: C, C, 67.62; H, 6.69.

4.3.5. 3-(3-Fluoro-1-hydroxybut-3-enyl)phenol ***2e*** *(Table 2, entry 5).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.18 (m, 1H), 6.98–6.85 (m, 2H), 6.76 (dd, J=8.0, 2.5 Hz, 1H), 4.96 (br s, 1H), 4.96–4.86 (m, 1H), 4.66 (dd, J=17.4, 2.8 Hz, 1H), 4.35 (dd, J=50.0, 2.8 Hz, 1H), 2.72–2.49 (m, 2H), 2.02 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (d, J=257 Hz), 155.8, 145.0, 129.9, 118.1, 114.8, 112.5, 92.9 (d, J=19 Hz), 70.6, 42.2 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.0 (dddd, J=34, 21, 20, 17 Hz). IR (cm^{-1}): 3327, 3077, 2921, 1464, 1030, 854. Anal. Calcd for $C_{10}H_{11}FO_2$: C, 65.92; H, 6.09. Found: C, 65.59; H, 6.00.

4.3.6. (E)-5-Fluoro-2-methyl-1-phenylhexa-1,5-dien-3-ol ***2f*** *(Table 2, entry 6).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.08 (m, 5H), 6.50 (s, 1H), 4.60 (dd, J=17.3, 2.4 Hz, 1H), 4.46–4.21 (m, 2H), 2.56–2.34 (m, 2H), 2.01 (s, 1H), 1.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (d, J=257 Hz), 138.7, 137.2, 129.0 (2C), 128.2 (2C), 126.6, 126.4, 92.6 (d, J=19 Hz), 74.3, 38.7 (d, J=26 Hz), 13.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.4 (ddt, J=50, 21, 17 Hz). IR (cm^{-1}): 2918, 1673, 748, 697. Anal. Calcd for $C_{13}H_{15}FO$: C, 75.70; H, 7.33. Found: C, 75.79; H, 7.13.

4.3.7. 3-Fluoro-1-(thiophen-2-yl)but-3-en-1-ol ***2g*** *(Table 2, entry 7).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J=5.1 Hz, 1H), 6.98–6.85 (m, 2H), 5.15 (t, J=6.6 Hz, 1H), 4.60 (dd, J=17.3, 2.9 Hz, 1H), 4.31 (dd, J=49.9, 2.7 Hz, 1H), 2.79–2.56 (m, 2H), 2.25 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (d, J=257 Hz), 146.7, 126.7, 124.9, 124.0, 93.2 (d, J=19 Hz), 67.0, 42.4 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.2 (ddt, J=50, 20, 17 Hz). IR (cm^{-1}): 3297, 2921, 1678, 1057. Anal. Calcd for C_8H_9FOS: C, 55.79; H, 5.27; S, 18.62. Found: C, 55.56; H, 4.95; S, 18.43.

4.3.8. 3-Fluoro-1-(pyridin-3-yl)but-3-en-1-ol ***2h*** *(Table 2, entry 8).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.55 (d, J=3.7 Hz, 1H), 7.74 (dt, J=7.8, 1.8 Hz, 1H), 7.30 (dd, J=7.8, 4.8 Hz, 1H), 5.02 (dd, J=7.7, 5.6 Hz, 1H), 4.69 (dd, J=17.2, 3.0 Hz, 1H), 4.36 (dd, J=49.8, 2.9 Hz, 1H), 2.81–2.55 (m, 2H), 2.44 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (d, J=257 Hz), 149.1, 147.6, 138.8, 133.8, 123.7, 93.5 (d, J=19 Hz), 68.7, 42.4 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.0 (ddt, J=50, 22, 17 Hz). IR (cm^{-1}): 2918, 1677, 1428, 855, 712. Anal. Calcd for $C_9H_{10}FNO$: C, 64.66; H, 6.03; N, 8.38. Found: C, 65.01; H, 6.01; N, 8.35.

4.3.9. 1-(2-Amino-4,6-dichloropyrimidin-5-yl)-3-fluorobut-3-en-1-ol ***2i*** *(Table 2, entry 9).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (s, 2H), 5.53–5.42 (m, 1H), 4.65 (d, J=16.9 Hz, 1H), 4.39 (d, J=49.2 Hz, 1H), 2.96 (ddd, J=22.6, 14.5, 8.2 Hz, 1H), 2.85–2.68 (m, 1H), 2.67 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (d, J=258 Hz), 161.5 (2C), 160.4, 119.8, 93.5 (d, J=17 Hz), 67.1 (d, J=2 Hz), 38.3 (d, J=27 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −96.0 (dq, J=50, 17 Hz). IR (cm^{-1}): 3320, 1637, 1567, 1505, 806, 444. Anal. Calcd for $C_8H_8Cl_2FN_3O$: C, 38.12; H, 3.20; N, 16.67. Found: C, 37.78; H, 3.34; N, 16.97.

4.3.10. 3-Fluoro-1-ferrocenylbut-3-en-1-ol ***2j*** *(Table 2, entry 10).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63–4.49 (m, 2H), 4.39–4.17 (m, 1H), 4.20 (s, 1H), 4.16–4.04 (m, 8H), 2.58–2.37 (m, 2H), 2.08 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7 (d, J=257 Hz), 92.6, 92.3 (d, J=20 Hz), 68.6 (5C), 68.3, 68.2, 67.1, 66.6, 65.6, 41.2 (d, J=26 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.4 (m). IR (cm^{-1}): 3099, 2922, 1673, 849, 816, 477. Anal. Calcd for $C_{14}H_{15}FFeO$: C, 61.34; H, 5.52. Found: C, 61.12; H, 5.72.

4.3.11. 5-Fluoro-1-phenylhex-5-en-3-ol ***2k*** *(Table 2, entry 11).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.17 (m, 2H), 7.17–7.03 (m, 3H), 4.58 (dd, J=17.4, 2.8 Hz, 1H), 4.27 (dd, J=50.1, 2.7 Hz, 1H), 3.92–3.69 (m, 1H), 2.83–2.69 (m, 1H), 2.69–2.54 (m, 1H), 2.46–2.13 (m, 2H), 1.82–1.66 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7 (d, J=257 Hz), 141.8, 128.60 (2C), 128.56 (2C), 126.1, 92.8 (d, J=20 Hz), 68.0, 40.5 (d, J=26 Hz), 38.5, 32.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −94.5 (dddd, J=50, 24, 17, 16 Hz). IR (cm^{-1}): 3376, 2922, 1673, 848, 698. Anal. Calcd for $C_{12}H_{15}FO$: C, 74.20; H, 7.78. Found: C, 74.41; H, 7.75.

4.3.12. 2-Fluorododec-1-en-4-ol ***2l*** *(Table 2, entry 12).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (dd, J=17.4, 2.7 Hz, 1H), 4.35 (dd, J=50.1, 2.7 Hz, 1H), 3.93–3.77 (m, 1H), 2.47–2.15 (m, 2H), 1.55-1.40 (m, 2H), 1.38–1.17 (m, 12H), 0.88 (t, J=6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (d, J=258 Hz), 92.5 (d, J=22 Hz), 68.5, 40.3 (d, J=27 Hz), 36.8, 31.9, 29.7, 29.5, 29.2, 25.5, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −94.6 (dddd, J=50, 24, 17, 15 Hz). IR (cm^{-1}): 3346, 2943, 1215, 1018, 838, 702. Anal. Calcd for $C_{12}H_{23}FO$: C, 71.24; H, 11.46. Found: C, 70.92; H, 11.54.

4.3.13. (6S)-2-Fluoro-6,10-dimethylundeca-1,9-dien-4-ol ***2m*** *(Table 2, entry 13).* Procedure A. Mixture 50:50 of diastereoisomers. ^{1}H

NMR (300 MHz, $CDCl_3$) δ 5.03 (t, J=6.9 Hz, 1H), 4.58 (dd, J=17.4, 1.5 Hz, 1H), 4.28 (d, J=50.3 Hz, 1H), 3.92 (br s, 1H), 2.44–2.04 (m, 2H), 2.05–1.81 (m, 2H), 1.78–1.57 (m, 1H), 1.61 (s, 3H), 1.53 (s, 3H), 1.46–1.21 (m, 3H), 1.23–1.01 (m, 2H), 0.92–0.71 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (d, J=257 Hz), 131.52 (0.5C), 131.46 (0.5C), 124.8, 92.9–92.3 (m), 66.7 (0.5C), 66.3 (0.5C), 44.4 (0.5C), 44.3 (0.5C), 41.2 (d, J=26 Hz, 0.5C), 40.7 (d, J=26 Hz, 0.5C), 37.9 (0.5C), 36.7 (0.5C), 29.4 (0.5C), 29.0 (0.5C), 25.9, 25.6 (0.5C), 25.4 (0.5C), 20.3 (0.5C), 19.2 (0.5C), 17.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −94.5 (m, 0.5F), −94.6 (m, 0.5F). IR (cm^{-1}): 3353, 2917, 1673, 845. Anal. Calcd for $C_{13}H_{23}FO$: C, 72.85; H, 10.82. Found: C, 73.23; H, 11.13.

4.3.14. 2-Fluoro-10-methoxy-6,10-dimethylundec-1-en-4-ol ***2n*** *(Table 2, entry 14).* Procedure A. Mixture 50:50 of diastereoisomers. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70–4.57 (m, 1H), 4.41–4.26 (m, 1H), 4.01–3.87 (m, 1H), 3.17 (s, 3H), 2.47–2.14 (m, 2H), 1.78–1.57 (m, 1H), 1.55–1.17 (m, 9H), 1.13 (s, 6H), 1.00–0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J=257 Hz), 92.4 (d, J=19 Hz), 74.7, 66.6 (0.5C), 66.2 (0.5C), 49.1, 44.4 (0.5C), 44.2 (0.5C), 41.1 (d, J=26 Hz, 0.5C), 40.6 (d, J=26 Hz, 0.5C), 40.0, 38.3 (0.5C), 36.9 (0.5C), 29.5 (0.5C), 29.2 (0.5C), 25.0, 24.9, 21.2 (0.5C), 21.0 (0.5C), 20.2 (0.5C), 19.1 (0.5C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −94.47 (m, 0.5F), −94.52 (m, 0.5F). IR (cm^{-1}): 2938, 1676, 1080, 847, 737. Anal. Calcd for $C_{14}H_{27}FO_2$: C, 68.25; H, 11.05. Found: C, 68.37; H, 10.98.

4.3.15. (S)-Menthyl 4-fluoro-2-hydroxypent-4-enoate ***2o*** *(Table 2, entry 17).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.90–4.51 (m, 1.5H), 4.42 (br s, 0.5H), 4.26 (br s, 0.5H), 4.03 (br s, 0.5H), 3.05–2.89 (m, 1H), 2.78–2.35 (m, 2H), 2.06–1.86 (m, 1H), 1.85–1.69 (m, 1H), 1.69–1.54 (m, 2H), 1.52–1.25 (m, 2H), 1.25–1.08 (s, 1H), 1.13–0.90 (m, 2H), 0.90–0.76 (m, 7H), 0.76–0.61 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5 (0.5C), 173.5 (0.5C), 161.84 (d, J=257 Hz, 0.5C), 161.79 (d, J=257 Hz, 0.5C), 93.6–92.9 (m), 76.4 (0.5C), 75.9 (0.5C), 67.5 (0.5C), 67.2 (0.5C), 46.9, 40.8 (0.5C), 40.6 (0.5C), 37.3 (d, J=27 Hz, 0.5C), 37.0 (d, J=27 Hz, 0.5C), 34.1, 31.4, 26.2, 23.3, 22.0, 20.7, 16.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.7 (m, 0.5F), −96.1 (m, 0.5F). IR (cm^{-1}): 2955, 2926, 2872, 1731, 1214, 1094. Anal. Calcd for $C_{15}H_{25}FO_3$: C, 66.15; H, 9.25. Found: C, 68.01; H, 11.01.

4.3.16. (±)-(trans)-Methyl 1-(bis(tert-butoxycarbonyl)amino)-2-fluoro-2-(3-fluoro-1-hydroxybut-3-enyl)cyclopropanecarboxylate ***2p*** *(Table 2, entry 15).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (dd, J=17.2, 2.8 Hz, 1H), 4.42 (dd, J=49.7, 2.8 Hz, 1H), 4.35 (dtd, J=28.0, 7.1, 2.1 Hz, 1H), 3.94 (d, J=2.6 Hz, 1H), 3.77 (s, 3H), 2.79–2.57 (m, 2H), 2.23 (dd, J=18.1, 8.8 Hz, 1H), 1.81 (dd, J=22.6, 8.8 Hz, 1H), 1.53 (s, 9H), 1.49 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 162.9 (d, J=256 Hz), 153.9, 151.5, 92.5 (d, J=23 Hz), 86.3 (d, J=237 Hz), 84.4, 83.4, 66.5 (d, J=20 Hz), 53.2 (d, J=4 Hz), 44.3 (d, J=9 Hz), 35.8 (d, J=26 Hz), 27.9 (6C), 27.1 (d, J=9.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.6 (m), −190.1 (dddd, J=28, 22, 18, 2 Hz). IR (cm^{-1}): 3480, 2980, 1735, 1678, 1120. Anal. Calcd for $C_{19}H_{29}F_2NO_7$: C, 54.15; H, 6.94; N, 3.32. Found: C, 54.38; H, 7.02; N, 3.62.

4.3.17. (±)-(trans)-Methyl 1-(bis(tert-butoxycarbonyl)amino)-2-fluoro-2-(3-fluoro-1-hydroxybut-3-enyl)cyclopropanecarboxylate ***2q*** *(Table 2, entry 16).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18–4.96 (m, 2H), 4.74 (dd, J=17.0, 3.0 Hz, 1H), 4.45 (dd, J=49.6, 3.0 Hz, 1H), 3.75 (s, 3H), 3.00–2.67 (m, 2H), 2.46 (dd, J=20.8, 8.2 Hz, 1H), 1.71 (dd, J=13.2, 8.3 Hz, 1H), 1.49 (s, 9H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 161.3 (d, J=254 Hz), 155.5, 152.9, 94.1 (d, J=17 Hz), 83.9 (d, J=240 Hz), 83.3, 81.0, 73.3 (d, J=21 Hz), 52.9 (d, J=4 Hz), 43.5 (d, J=10 Hz), 33.4 (dd, J=28, 6 Hz), 29.7, 28.2 (3C), 27.7 (3C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −95.8 (ddddd, J=50, 26, 17, 11, 1 Hz), −190.5 (dt, J=22, 12 Hz). IR (cm^{-1}): 2921, 1739, 1249, 1157. Anal. Calcd for $C_{19}H_{29}F_2NO_7$: C, 54.15; H, 6.94; N, 3.32. Found: C, 53.75; H, 6.89; N, 3.61.

4.3.18. 4-Fluoro-2-phenylpent-4-en-2-ol ***2r*** *(Table 2, entry 18).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J=7.9 Hz, 2H), 7.28 (t, J=7.5 Hz, 2H), 7.19 (t, J=7.2 Hz, 1H), 4.56 (dd, J=17.5, 2.2 Hz, 1H), 4.17 (dd, J=50.1, 2.3 Hz, 1H), 2.75–2.50 (m, 2H), 2.20 (d, J=2.1 Hz, 1H), 1.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, J=258 Hz), 146.8, 128.2 (2C), 127.0, 124.6 (2C), 94.2 (d, J=20 Hz), 73.3 (d, J=3 Hz), 46.6 (d, J=24 Hz), 29.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ −89.6 (dq, J=50, 20 Hz). IR (cm^{-1}): 3392, 2928, 1674, 1167, 854. Anal. Calcd for $C_{11}H_{13}FO$: C, 73.31; H, 7.27. Found: C, 73.34 H, 7.53.

4.3.19. 1,1,1,4-Tetrafluoro-2-phenylpent-4-en-2-ol ***2s*** *(Table 2, entry 19).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J=7.0 Hz, 2H), 7.47–7.33 (m, 3H), 4.66 (dd, J=17.4, 2.7 Hz, 1H), 4.31 (dd, J=49.8, 2.8 Hz, 1H), 3.24 (br s, 1H), 3.19–2.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3 (d, J=257 Hz), 135.9, 128.8, 128.3 (2C), 126.3 (2C), 125.0 (q, J=286 Hz), 95.9 (d, J=19 Hz), 76.0 (qd, J=28, 2 Hz), 38.6 (d, J=25 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.6 (m, 3F), −90.7 (m). IR (cm^{-1}): 3346, 2945, 1674, 1167, 1018, 851, 701. Anal. Calcd for $C_{11}H_{10}F_4O$: C, 56.41; H, 4.30. Found: C, 56.65; H, 4.45.

4.3.20. 1,1,1,5-Tetrafluoro-3-phenylhex-5-en-3-ol ***2t*** *(Table 2, entry 20).* Procedure A. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.10 (m, 5H), 4.68 (dd, J=17.3, 2.6 Hz, 1H), 4.34 (dd, J=49.6, 2.5 Hz, 1H), 3.09 (d, J=14.2 Hz, 1H), 2.89 (d, J=14.2 Hz, 1H), 2.69–2.26 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (d, J=257 Hz), 133.9, 131.1 (2C), 128.6 (2C), 127.5, 125.7 (q, J=287 Hz), 95.5 (d, J=20 Hz), 74.9 (qd, J=27, 3 Hz), 39.8, 36.9 (d, J=25 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −78.9 (m, 3F), −91.5 (m). IR (cm^{-1}): 3360, 2942, 1674, 1164, 853, 701. Anal. Calcd for $C_{12}H_{12}F_4O$: C, 58.07; H, 4.87. Found: C, 57.84; H, 5.07.

4.3.21. (Z)-(3-Bromo-2-fluoroprop-1-enyl)benzene ***5a*** *(Table 3, entry 1).* Following procedure C, **5a** was obtained as a yellow oil in 88% yield, after flash chromatography (SiO_2, cyclohexane/EtOAc, 90:10, R_f=0.70 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58–7.31 (m, 5H), 5.90 (d, J=36.0 Hz, 1H), 4.14 (d, J=20.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5 (d, J=263 Hz), 132.3 (d, J=3 Hz), 129.1, 128.9, 128.7, 128.3, 128.2, 110.5 (d, J=8 Hz), 29.7 (d, J=31 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −108.3 (dt, J=36, 20 Hz). IR (cm^{-1}): 3027, 1681, 1422, 1351, 1205, 904, 690. Anal. Calcd for C_9H_8BrF: C, 50.26; H, 3.75. Found: C, 50.45; H, 3.59.

4.3.22. (Z)-(5-Bromo-4-fluoropent-3-enyl)benzene ***5b*** *(Table 3, entry 2).* Following procedure C, **5b** was obtained as a yellow oil in 50% yield, after flash chromatography (SiO_2, cyclohexane/EtOAc, 90:10, R_f=0.78 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.13 (m, 5H), 5.01 (dt, J=34.3, 7.5 Hz, 1H), 3.94 (d, J=19.6 Hz, 2H), 2.72 (t, J=7.6 Hz, 2H), 2.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6 (d, J=251 Hz), 141.2, 128.64 (2C), 128.61 (2C), 126.3, 110.3 (d, J=15 Hz), 35.1 (d, J=1 Hz), 28.8 (d, J=32 Hz), 25.9 (d, J=3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −114.5 (dtt, J=34, 19, 1 Hz). IR (cm^{-1}): 3027, 1691, 1454, 1233, 697. Anal. Calcd for $C_{11}H_{12}BrF$: C, 54.34; H, 4.98. Found: C, 53.25; H, 5.07.

4.3.23. (Z)-1-Bromo-4-(3-bromo-2-fluoroprop-1-enyl)benzene ***5c*** *(Table 3, entry 3).* Following procedure C, **5c** was obtained as a colorless oil in 91% yield, after flash chromatography (SiO_2, cyclohexane/EtOAc, 90:10, R_f=0.73 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J=8.3 Hz, 2H), 7.38 (d, J=8.2 Hz, 2H), 5.82 (d, J=35.6 Hz, 1H), 4.12 (d, J=20.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0 (d, J=264 Hz), 131.8 (2C), 131.2 (d, J=4 Hz), 130.5, 130.4, 122.1, 109.4 (d, J=8 Hz), 29.4 (d, J=31 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −106.9 (dt, J=35, 20 Hz). IR (cm^{-1}): 1676, 1486, 1235, 1159,

1008, 857, 808, 661. Anal. Calcd for $C_9H_7Br_2F$: C, 36.77; H, 2.40. Found: C, 36.55; H, 2.50.

4.3.24. (Z)-1-(3-Bromo-2-fluoroprop-1-enyl)-4-methoxybenzene ***5d*** *(Table 3, entry 4).* Following procedure C, **5d** was obtained as a crude colorless oil in 84% yield (R_f=0.68 cyclohexane/EtOAc 8:2). The compound was unstable on SiO_2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J=8.4 Hz, 2H), 6.90 (d, J=8.5 Hz, 2H), 5.84 (d, J=36.4 Hz, 1H), 4.15 (d, J=20.4 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 153.1 (d, J=260 Hz), 130.5, 130.4, 125.0 (d, J=4 Hz), 114.0 (2C), 110.2 (d, J=8 Hz), 55.3, 30.3 (d, J=31 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −111.3 (dt, J=36, 20 Hz). IR (cm^{-1}): 1679, 1606, 1510, 1463, 1237, 1176, 1154, 1029.

4.3.25. 1-(4-Chlorophenyl)-3-fluoro-2-phenylbut-3-en-1-ol ***6a*** *(Table 5, entry 1).* Following procedure D, **6a** was obtained as the pure *anti* (white solid) and the pure *syn* (colorless oil) diastereomers, after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 65:35). Compound **6a** *anti*: R_f=0.42 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16–6.91 (m, 9H), 4.99 (d, J=9.4 Hz, 1H), 4.73 (dd, J=17.8, 3.1 Hz, 1H), 4.55 (dd, J=50.1, 3.1 Hz, 1H), 3.58 (dd, J=24.8, 9.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7 (d, J=258 Hz), 139.7, 136.9, 133.5, 128.5, 128.4, 128.4, 128.3, 128.1, 127.4, 93.4 (d, J=20 Hz), 74.4 (d, J=3 Hz), 57.8 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.6 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3385, 2932, 1675, 1492, 1451, 1236, 1030, 1010. Anal. Calcd for $C_{16}H_{14}ClFO$: C, 69.44; H, 5.10. Found: C, 69.63; H, 5.25. Compound **6a** *syn*: R_f=0.51 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 9H), 5.12 (dd, J=8.5, 2.6 Hz, 1H), 4.40 (dd, J=17.9, 3.1 Hz, 1H), 4.16 (dd, J=50.2, 3.1 Hz, 1H), 3.54 (dd, J=23.9, 8.5 Hz, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4 (d, J=260 Hz), 140.0, 136.8, 133.7, 128.9, 128.9, 128.8, 128.5, 128.4, 128.2, 128.0, 127.9, 93.0 (d, J=19 Hz), 73.8 (d, J=1 Hz), 58.0 (d, J=23 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.2 (ddd, J=50, 24, 18 Hz). IR (cm^{-1}): 3270, 2973, 1670, 1492, 1243, 1047, 1012. Anal. Calcd for $C_{16}H_{14}ClFO$: C, 69.44; H, 5.10. Found: C, 69.79; H, 4.99.

4.3.26. 3-Fluoro-2-phenyl-1-(3,4,5-trimethoxyphenyl)but-3-en-1-ol ***6b*** *(Table 5, entry 2).* Following procedure D, **6b** was obtained as a mixture of *anti*/*syn* diastereomers (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30, R_f=0.14 cyclohexane/EtOAc 8:2). Compound **6b** *anti*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–6.91 (m, 5H), 6.17 (s, 2H), 4.89 (d, J=9.5 Hz, 1H), 4.71 (dd, J=17.8, 3.1 Hz, 1H), 4.54 (dd, J=50.2, 3.1 Hz, 1H), 3.66 (s, 3H), 3.56 (s, 6H), 3.48 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (d, J=262 Hz), 152.6, 137.5, 137.5, 137.0 (2C), 128.6, 128.5, 128.3 (2C), 127.2, 103.5 (2C), 93.0 (d, J=20 Hz), 75.0 (d, J=3 Hz), 60.8, 58.0 (d, J=24 Hz), 55.9, 55.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.4 (ddd, J=50, 25, 18 Hz). Compound **6b** *syn*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–6.91 (m, 5H), 6.44 (s, 2H), 5.06 (d, J=7.9 Hz, 1H), 4.42 (dd, J=18.5, 3.2 Hz, 1H), 4.22 (dd, J=50.5, 3.1 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 6H), 3.56 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (d, J=260 Hz), 152.9, 137.4, 137.3, 137.1 (2C), 129.1 (2C), 128.7 (2C), 127.7, 103.5 (2C), 92.8 (d, J=19 Hz), 74.4, 60.8, 57.7 (d, J=22 Hz), 56.1, 56.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.8 (ddd, J=50, 22, 18 Hz). IR (cm^{-1}): 3446, 2943, 1669, 1590, 1454, 1420, 1328, 1233, 1127, 1003. Anal. Calcd for $C_{19}H_{21}FO_4$: C, 68.66; H, 6.37. Found: C, 68.77; H, 6.51.

4.3.27. 1-(Benzo[d][1,3]dioxol-5-yl)-3-fluoro-2-phenylbut-3-en-1-ol ***6c*** *(Table 5,entry 3).* Following procedure D, **6c** was obtained as the pure *anti* diastereomer (yellow oil) and the mixture of *anti*/*syn* diastereomers (yellow oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6c** *anti*: R_f=0.28 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13–6.95 (m, 5H), 6.63 (s, 1H), 6.54–6.37 (m, 2H), 5.78 (d, J=2.9 Hz, 2H), 4.91 (dd, J=9.5, 2.3 Hz, 1H), 4.70 (dd, J=17.8, 3.0 Hz, 1H), 4.53 (dd, J=50.1, 3.0 Hz, 1H), 3.58 (dd, J=25.0, 9.5 Hz, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (d, J=262 Hz), 147.5, 147.0, 137.4 (d, J=2 Hz), 135.3, 128.5, 128.4, 128.4 (2C), 127.3, 120.6, 107.8, 106.9, 100.9, 93.0 (d, J=20 Hz), 74.8 (d, J=3 Hz), 57.7 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.6 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3028, 2897, 1670, 1487, 1442, 1240, 1034. Anal. Calcd for $C_{17}H_{15}FO_3$: C, 71.32; H, 5.28. Found: C, 71.13; H, 5.39. Compound **6c** *syn*: R_f=0.32 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.20 (m, 5H), 6.83–6.66 (m, 3H), 5.86 (s, 2H), 5.03 (d, J=8.6 Hz, 1H), 4.37 (dd, J=17.9, 3.0 Hz, 1H), 4.15 (dd, J=50.2, 3.1 Hz, 1H), 3.54 (dd, J=24.3, 8.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 (d, J=260 Hz), 147.7, 147.2, 137.3 (d, J=2 Hz), 135.6, 128.9 (2C), 128.8, 128.8, 127.8, 120.3, 108.0, 106.9, 101.1, 92.7 (d, J=19 Hz), 74.3, 58.0 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.1 (ddd, J=50, 24, 18 Hz). IR (cm^{-1}): 3027, 2893, 1669, 1487, 1442, 1241, 1034. Anal. Calcd for $C_{17}H_{15}FO_3$: C, 71.32; H, 5.28. Found: C, 71.61; H, 5.41.

4.3.28. 3-Fluoro-2-phenyl-1-(thiophen-2-yl)but-3-en-1-ol ***6d*** *(Table 5,entry 4).* Following procedure D, **6d** was obtained as the pure *anti* diastereomer (yellow oil) and the mixture of *anti*/*syn* diastereomers (yellow oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6d** *anti*: R_f=0.41 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.13 (m, 6H), 6.85–6.74 (m, 1H), 6.66 (d, J=3.4 Hz, 1H), 5.42 (dd, J=9.4, 3.2 Hz, 1H), 4.82 (dd, J=17.7, 3.1 Hz, 1H), 4.67 (dd, J=50.0, 3.1 Hz, 1H), 3.80 (dd, J=24.9, 9.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5 (d, J=262 Hz), 144.9, 137.2 (d, J=2 Hz), 128.5 (2C), 128.4, 128.4, 127.5, 126.4, 125.3, 124.9, 93.3 (d, J=19 Hz), 70.9, 58.1 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −102.4 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3411, 2922, 1670, 1248, 1034. Anal. Calcd for $C_{14}H_{13}FOS$: C, 67.72; H, 5.28; S, 12.91. Found: C, 667.75; H, 5.53; S, 13.00. Compound **6d** *syn*: R_f=0.51 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (m, 6H), 6.96 (d, J=3.3 Hz, 1H), 6.92–6.84 (m, 1H), 5.42 (dd, J=8.5, 3.2 Hz, 1H), 4.45 (dd, J=17.9, 3.1 Hz, 1H), 4.25 (dd, J=50.2, 3.1 Hz, 1H), 3.68 (dd, J=22.9, 8.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5 (d, J=261 Hz), 145.1, 136.9, 128.9 (4C), 127.9, 126.5, 125.3, 125.1, 92.9 (d, J=19 Hz), 70.6, 58.31 (d, J=22 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.5 (ddd, J=50, 23, 18 Hz). IR (cm^{-1}): 2921, 1670, 1494, 1248, 1033. Anal. Calcd for $C_{14}H_{13}FOS$: C, 67.72; H, 5.28; S, 12.91. Found: C, 68.00; H, 5.36; S, 13.13.

4.3.29. (E)-2-Fluoro-3-phenylhepta-1,5-dien-4-ol ***6e*** *(Table 5,entry 5).* Following procedure D, **6e** was obtained as the pure *anti* diastereomer (colorless oil) and the mixture of *anti*/*syn* diastereomers (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6e** *anti*: R_f=0.44 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.18 (m, 5H), 5.72–5.53 (m, 1H), 5.50–5.31 (m, 1H), 4.76 (dd, J=17.9, 2.9 Hz, 1H), 4.58 (dd, J=50.3, 3.0 Hz, 1H), 4.55 (t, J=7.5 Hz, 1H), 3.51 (dd, J=23.4, 8.5 Hz, 1H), 1.60 (d, J=6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (d, J=261 Hz), 137.6, 130.8, 129.0, 128.7 (2C), 128.5 (2C), 127.4, 92.9 (d, J=20 Hz), 72.9, 56.0 (d, J=24 Hz), 17.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.6 (ddd, J=50, 23, 18 Hz). IR (cm^{-1}): 3395, 3030, 2918, 1668, 1452, 1254, 1035. Anal. Calcd for $C_{13}H_{15}FO$: C, 75.70; H, 7.33. Found: C, 75.23; H, 77.44. Compound **6e** *syn*: R_f=0.51 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.24 (m, 5H), 5.91–5.75 (m, 1H), 5.63–5.51 (m, 1H), 4.66 (dd, J=18.1, 3.0 Hz, 1H), 4.58 (t, J=7.7 Hz, 1H), 4.46 (dd, J=50.4, 3.0 Hz, 1H), 3.50 (dd, J=21.7, 7.8 Hz, 1H), 1.75 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, J=260 Hz), 137.2, 130.9, 129.2, 128.9 (2C), 128.8 (2C), 127.7, 92.6 (d, J=20 Hz), 72.9, 55.9 (d, J=23 Hz), 17.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −99.7 (ddd, J=50, 22, 18 Hz). IR (cm^{-1}): 3390, 3033, 1669, 1452, 1251, 1032. Anal. Calcd for $C_{13}H_{15}FO$: C, 75.70; H, 7.33. Found: C, 75.82; H, 7.44.

4.3.30. 5-Fluoro-1,4-diphenylhex-5-en-3-ol ***6f*** *(Table 5,entry 6).* Following procedure D, **6f** was obtained as the pure *anti* diastereomer (white solid) and the pure *syn* diastereomer (colorless

oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6f** *anti*: R_f=0.44 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–6.96 (m, 10H), 4.64 (dd, J=17.7, 3.0 Hz, 1H), 4.45 (dd, J=50.2, 3.0 Hz, 1H), 4.09–3.94 (m, 1H), 3.35 (dd, J=25.4, 8.8 Hz, 1H), 2.84–2.69 (m, 1H), 2.60–2.50 (m, 1H), 1.72–1.46 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3 (d, J=262 Hz), 141.7, 137.9 (d, J=2 Hz), 128.8, 128.5, 128.4, 128.3, 128.3, 127.5, 125.9, 92.9 (d, J=20 Hz), 71.1, 56.4 (d, J=23 Hz), 36.1, 31.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.0 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3413, 3033, 2910, 1673, 1493, 1451, 1252, 1080. Anal. Calcd for $C_{18}H_{19}FO$: C, 79.97; H, 7.08. Found: C, 79.91; H, 7.22. Compound **6f** *syn*: R_f=0.53 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.08 (m, 10H), 4.57 (dd, J=18.2, 3.0 Hz, 1H), 4.33 (dd, J=50.5, 3.0 Hz, 1H), 4.06 (t, J=8.3 Hz, 1H), 3.36 (dd, J=21.8, 7.6 Hz, 1H), 2.89–2.76 (m, 1H), 2.69–2.59 (m, 1H), 2.02–1.87 (m, 1H), 1.77–1.59 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6 (d, J=260 Hz), 141.9, 137.3, 128.9, 128.9, 128.5, 128.4, 127.7, 125.9, 92.5 (d, J=19 Hz), 70.9, 55.8 (d, J=23 Hz), 36.7, 32.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.1 (ddd, J=50, 22, 18 Hz). IR (cm^{-1}): 3027, 2926, 1667, 1495, 1453, 1244, 1072. Anal. Calcd for $C_{18}H_{19}FO$: C, 79.97; H, 7.08. Found: C, 79.73; H, 7.38.

4.3.31. 2-Fluoro-3-Phenyloct-1-en-4-ol ***6g*** *(Table 5,entry 7).* Following procedure D, **6g** was obtained as the mixture *anti*/*syn* diastereomers (yellow oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6g** *anti*: R_f=0.55 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.13 (m, 5H), 4.64 (dd, J=17.9, 3.0 Hz, 1H), 4.46 (dd, J=50.3, 3.0 Hz, 1H), 4.12–3.91 (m, 1H), 3.32 (dd, J=25.5, 8.5 Hz, 1H), 1.47–1.06 (m, 6H), 0.75 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (d, J=262 Hz), 138.2 (d, J=2 Hz), 129.0, 128.7 (2C), 128.3, 127.4, 92.7 (d, J=20 Hz), 71.8, 56.3 (d, J=23 Hz), 34.1, 27.7, 22.5, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.7 (ddd, J=50, 25, 18 Hz). Compound **6g** *syn*: R_f=0.60 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.13 (m, 5H), 4.58 (dd, J=17.9, 2.4 Hz, 1H), 4.38 (dd, J=50.6, 3.0 Hz, 1H), 4.12–3.91 (m, 1H), 3.34 (dd, J=21.3, 7.1 Hz, 1H), 1.47–1.06 (m, 6H), 0.81 (t, 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (d, J=260 Hz), 137.5, 129.0, 128.8 (2C), 128.3, 127.6, 92.3 (d, J=20 Hz), 71.5, 55.7 (d, J=24 Hz), 34.6, 27.9, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −99.7, −100.1 (m). IR (cm^{-1}): 2956, 2936, 1668, 1494, 1454, 1254. Anal. Calcd for $C_{14}H_{19}FO$: C, 75.64; H, 8.61. Found: C, 75.42; H, 8.48.

4.3.32. 2-Fluoro-3-phenyldodec-1-en-4-ol ***6h*** *(Table 5,entry 8).* Following procedure D, **6h** was obtained as the pure *anti* diastereomer (colorless oil) and the pure *syn* diastereomer (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6h** *anti*: R_f=0.58 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.08 (m, 5H), 4.65 (d, J=17.8 Hz, 1H), 4.47 (d, J=50.3 Hz, 1H), 4.09–3.90 (m, 1H), 3.32 (dd, J=25.3, 8.7 Hz, 1H), 1.42–1.06 (m, 14H), 0.79 (t, J=6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (d, J=261 Hz), 138.2, 128.7 (2C), 128.3 (2C), 127.4, 92.7 (d, J=20 Hz), 71.7, 56.3 (d, J=23 Hz), 34.4, 31.8, 29.5, 29.4, 29.2, 25.5, 22.6, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.8 (ddd, J=50, 25, 17 Hz). IR (cm^{-1}): 3435, 2917, 2851, 1669, 1466, 1454, 1250, 1081. Anal. Calcd for $C_{18}H_{27}FO$: C, 77.65; H, 9.78. Found: C, 77.96; H, 9.88. Compound **6h** *syn*: R_f=0.69 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.11 (m, 5H), 4.59 (d, J=18.2 Hz, 1H), 4.39 (d, J=50.6 Hz, 1H), 4.15–3.93 (m, 1H), 3.34 (dd, J=21.4, 7.4 Hz, 1H), 1.62–1.08 (m, 14H), 0.81 (t, J=6.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 (d, J=260 Hz), 137.4, 129.0 (2C), 128.8 (2C), 127.6, 92.32 (d, J=20 Hz), 71.5, 55.7 (d, J=23 Hz), 34.9, 31.9, 29.6 (2C), 29.3, 25.7, 22.7, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.0 (ddd, J=50, 21, 18 Hz). IR (cm^{-1}): 3430, 2923, 2853, 1667, 1463, 1189. Anal. Calcd for $C_{18}H_{27}FO$: C, 77.65; H, 9.78. Found: C, 77.99; H, 9.66.

4.3.33. 1-(4-Chlorophenyl)-3-fluoro-2-phenethylbut-3-en-1-ol ***6i*** *(Table 5, entry 9).* Following procedure D, **6i** was obtained as the pure *anti* diastereomer (colorless oil) and the mixture of *anti*/*syn* diastereomers (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6i** *anti*: R_f=0.40 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41–6.96 (m, 9H), 4.87 (ddd, J=17.7, 2.8, 0.7 Hz, 1H), 4.65 (d, J=8.7 Hz, 1H), 4.47 (dd, J=50.5, 2.9 Hz, 1H), 2.85–2.65 (m, 1H), 2.60–2.36 (m, 2H), 1.87–1.64 (m, 1H), 1.50–1.32 (m, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3 (d, J=261 Hz), 141.2, 140.1, 133.8, 128.7 (2C), 128.4 (2C), 128.3 (2C), 128.2 (2C), 126.0, 94.7 (d, J=20 Hz), 73.9, 50.6 (d, J=24 Hz), 33.0, 28.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ −107.6 (ddd, J=50, 28, 18 Hz). IR (cm^{-1}): 3418, 2954, 1670, 1491, 1253, 1087, 1013. Anal. Calcd for $C_{18}H_{18}ClFO$: C, 70.93; H, 5.95. Found: C, 71.15; H, 6.17. Compound **6i** *syn*: R_f=0.51 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–6.97 (m, 9H), 4.79 (d, J=6.9 Hz, 1H), 4.62 (dd, J=18.1, 3.0 Hz, 1H), 4.18 (dd, J=50.9, 3.0 Hz, 1H), 2.86–2.66 (m, 1H), 2.61–2.38 (m, 2H), 2.16–1.99 (m, 1H), 1.97–1.79 (m, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (d, J=259 Hz), 141.6, 140.7, 133.4, 128.4 (4C), 128.3 (2C), 127.6 (2C), 125.9, 93.5 (d, J=20 Hz), 74.4, 50.5 (d, J=23 Hz), 33.3, 28.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −103.5 (ddd, J=51, 26, 18 Hz). IR (cm^{-1}): 3420, 2920, 1671, 1452, 1244, 1125. Anal. Calcd for $C_{18}H_{18}ClFO$: C, 70.93; H, 5.95. Found: C, 71.12; H, 6.20.

4.3.34. (E)-2-Fluoro-3-phenethylhepta-1,5-dien-4-ol ***6j*** *(Table 5,entry 10).* Following procedure D, **6j** was obtained as the mixture of *anti*/*syn* diastereomer (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30, R_f=0.43 and 0.47 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.05 (m, 10H), 5.73–5.54 (m, 2H), 5.49–5.25 (m, 2H), 4.71 (dd, J=20.8, 2.8 Hz, 1H), 4.65 (dd, J=21.1, 2.8 Hz, 1H), 4.34 (dd, J=50.6, 2.8 Hz, 1H), 4.28 (dd, J=50.7, 2.8 Hz, 1H), 4.08–3.93 (m, 2H), 2.79–2.59 (m, 2H), 2.58–2.37 (m, 2H), 2.36–2.02 (m, 2H), 1.89–1.60 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (d, J=261 Hz), 164.9 (d, J=261 Hz), 141.8, 141.7, 131.3, 131.2, 129.8, 128.5 (2C), 128.4 (2C), 128.4 (5C), 126.0, 125.9, 93.8 (d, J=21 Hz), 93.3 (d, J=20 Hz), 73.8, 73.3, 49.2 (d, J=24 Hz), 48.8 (d, J=23 Hz), 33.3, 33.3, 29.4, 29.0, 17.8 (2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −102.2 (ddd, J=51, 27, 18 Hz), −105.9 (ddd, J=51, 28, 18 Hz). IR (cm^{-1}): 3420, 3021, 2932, 1668, 1452, 1250, 1001. Anal. Calcd for $C_{15}H_{19}FO$: C, 76.89; H, 8.17. Found: C, 76.66; H, 8.13.

4.3.35. 2-Fluoro-3-phenethyloct-1-en-4-ol ***6k*** *(Table 5,entry 11).* Following procedure D, **6k** was obtained as the mixture of *anti*/*syn* diastereomers (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30, R_f=0.55 cyclohexane/EtOAc 8:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.13 (m, 10H), 4.81 (dd, J=17.9, 2.4 Hz, 1H), 4.76 (dd, J=18.3, 2.5 Hz, 1H), 4.41 (dd, J=51.1, 2.8 Hz, 1H), 4.39 (dd, J=50.9, 2.8 Hz, 1H), 3.65 (br s, 2H), 2.90–2.72 (m, 2H), 2.70–2.50 (m, 2H), 2.39–2.17 (m, 2H), 2.02–1.76 (m, 4H), 1.72–1.25 (m, 12H), 0.93 (t, J=6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (d, J=261 Hz), 165.5 (d, J=261 Hz), 141.9, 141.7, 128.5 (2C), 128.4 (2C), 128.4 (2C), 128.4 (2C), 126.0, 125.9, 93.6 (d, J=20 Hz), 92.9 (d, J=20 Hz), 72.6, 72.0, 48.9 (d, J=23 Hz), 48.6 (d, J=23 Hz), 34.4, 34.2, 33.4 (2C), 29.8, 28.7, 28.1, 27.8, 22.7, 22.6, 14.1 (2C). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.9 (ddd, J=51, 28, 18 Hz), −102.7 (ddd, J=51, 27, 18 Hz). IR (cm^{-1}): 3450, 2955, 2931, 1667, 1454, 1251, 1001. Anal. Calcd for $C_{16}H_{23}FO$: C, 76.76; H, 9.26. Found: C, 76.33; H, 9.19.

4.3.36. 2-(4-Bromophenyl)-1-(4-chlorophenyl)-3-fluorobut-3-en-1-ol ***6l*** *(Table 5, entry 12).* Following procedure D, **6l** was obtained as the pure *anti* diastereomer (colorless oil) and the pure *syn* diastereomer (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6l** *anti*: R_f=0.43 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.19 (m, 2H), 7.14–7.03 (m, 2H), 7.02–6.90 (m, 2H), 6.90–6.79 (m, 2H), 4.92 (d, J=9.4 Hz, 1H), 4.73 (dd, J=17.7, 3.2 Hz, 1H), 4.54 (dd, J=50.0, 3.2 Hz, 1H), 3.53 (dd, J=24.7, 9.4 Hz, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (d, J=262 Hz), 139.4, 136.0 (d, J=2 Hz), 133.7, 131.6 (2C),

130.2, 130.1, 128.4 (2C), 128.1 (2C), 121.5, 93.7 (d, J=20 Hz), 74.1 (d, J=3 Hz), 57.2 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −102.3 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3401, 1670, 1487, 1255, 1088, 1010. Anal. Calcd for $C_{16}H_{13}BrClFO$: C, 54.04; H, 3.68. Found: C, 54.32; H, 3.78. Compound **6l** *syn*: R_f=0.57 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.36 (m, 2H), 7.28–7.13 (m, 6H), 5.12 (d, J=7.9 Hz, 1H), 4.44 (dd, J=18.0, 3.3 Hz, 1H), 4.17 (dd, J=50.3, 3.2 Hz, 1H), 3.52 (dd, J=22.5, 7.9 Hz, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (d, J=260 Hz), 139.9, 135.8, 133.8, 131.8 (2C), 130.7, 130.7, 128.5 (2C), 127.8 (2C), 121.9, 93.4 (d, J=19 Hz), 73.6, 57.1 (d, J=24 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.3 (ddd, J=50, 22, 18 Hz). IR (cm^{-1}): 3400, 1671, 1487, 1249, 1089, 1073, 1011. Anal. Calcd for $C_{16}H_{13}BrClFO$: C, 54.04; H, 3.68. Found: C, 54.99; H, 4.08.

4.3.37. (E)-3-(4-Bromophenyl)-2-fluorohepta-1,5-dien-4-ol **6m** *(Table 5,entry 13).* Following procedure D, **6m** was obtained as the pure *anti* diastereomer (colorless oil) and the pure *syn* diastereomer (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6m** *anti*: R_f=0.37 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J=8.5 Hz, 2H), 7.07 (d, J=8.3 Hz, 2H), 5.65–5.43 (m, 1H), 5.36–5.16 (m, 1H), 4.67 (dd, J=17.8, 3.1 Hz, 1H), 4.47 (dd, J=50.2, 3.1 Hz, 1H), 4.40 (t, J=7.7 Hz, 1H), 3.37 (dd, J=23.4, 8.5 Hz, 1H), 1.51 (dd, J=6.5, 0.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5 (d, J=261 Hz), 136.7, 131.6 (2C), 130.6, 130.4 (2C), 129.5, 121.3, 93.1 (d, J=20 Hz), 72.7, 55.4 (d, J=24 Hz), 17.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.3 (ddd, J=50, 23, 18 Hz). IR (cm^{-1}): 3396, 2915, 1669, 1487, 1254, 1073, 1010. Anal. Calcd for $C_{13}H_{14}BrFO$: C, 54.76; H, 4.95. Found: C, 55.08; H, 5.03. Compound **6m** *syn*: R_f=0.52 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J=8.5 Hz, 2H), 7.18 (d, J=8.4 Hz, 2H), 5.71 (dq, J=13.1, 6.4 Hz, 1H), 5.48–5.34 (m, 1H), 4.58 (dd, J=18.1, 3.1 Hz, 1H), 4.50–4.40 (m, 1H), 4.36 (dd, J=54.8, 4.5 Hz, 1H), 3.36 (dd, J=20.8, 7.5 Hz, 1H), 1.63 (dd, J=6.5, 1.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (d, J=260 Hz), 136.3, 131.7 (2C), 130.8, 130.7 (2C), 129.4, 121.6, 92.9 (d, J=20 Hz), 72.7, 55.1 (d, J=24 Hz), 17.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.1 (ddd, J=50, 21, 18 Hz). IR (cm^{-1}): 3390, 2915, 1669, 1487, 1250, 1074, 1010. Anal. Calcd for $C_{13}H_{14}BrFO$: C, 54.76; H, 4.95. Found: C, 55.40; H, 3.75.

4.3.38. 3-(4-Bromophenyl)-2-fluorooct-1-en-4-ol **6n** *(Table 5,entry 14).* Following procedure D, **6n** was obtained as the pure *anti* diastereomer (colorless oil) and the pure *syn* diastereomer (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30). Compound **6n** *anti*: R_f=0.42 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J=8.5 Hz, 2H), 7.09 (d, J=8.2 Hz, 2H), 4.66 (dd, J=17.7, 3.1 Hz, 1H), 4.46 (dd, J=50.2, 3.1 Hz, 1H), 3.94 (td, J=8.2, 3.4 Hz, 1H), 3.29 (dd, J=25.2, 8.6 Hz, 1H), 1.50–1.02 (m, 6H), 0.76 (t, J=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (d, J=262 Hz), 137.3 (d, J=2 Hz), 131.8 (2C), 130.0, 130.0, 121.4, 93.1 (d, J=20 Hz), 71.6, 55.7 (d, J=24 Hz), 34.2, 27.7, 22.5, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.4 (ddd, J=50, 25, 18 Hz). IR (cm^{-1}): 3346, 2937, 1674, 1488, 1244, 1079, 1010. Anal. Calcd for $C_{14}H_{18}BrFO$: C, 55.83; H, 6.02. Found: C, 56.13; H, 6.13. Compound **6n** *syn*: R_f=0.58 cyclohexane/EtOAc 8:2. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J=8.5 Hz, 2H), 7.18 (d, J=8.4 Hz, 2H), 4.60 (dd, J=18.2, 3.1 Hz, 1H), 4.36 (dd, J=50.5, 3.1 Hz, 1H), 4.02 (td, J=7.8, 3.2 Hz, 1H), 3.31 (dd, J=20.4, 7.0 Hz, 1H), 1.67–1.09 (m, 6H), 0.83 (t, J=7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (d, J=260 Hz), 136.5, 131.8 (2C), 130.8 (2C), 121.6, 92.7 (d, J=20 Hz), 71.3, 54.9 (d, J=24 Hz), 34.7, 27.9, 22.6, 14.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −100.4 (ddd, J=50, 20, 18 Hz). IR (cm^{-1}): 2933, 1669, 1487, 1243, 1073, 1010. Anal. Calcd for $C_{14}H_{18}BrFO$: C, 55.83; H, 6.02. Found: C, 56.09; H, 5.97.

4.3.39. 1-(4-Chlorophenyl)-3-fluoro-2-(4-methoxyphenyl)but-3-en-1-ol **6o** *(Table 5, entry 15).* Following procedure D, **6o** was obtained as the mixture of *anti*/*syn* diastereomers (colorless oil), after flash chromatography (SiO_2, cyclohexane/EtOAc, 95:5 to 70:30, R_f=0.42 cyclohexane/EtOAc 8:2). Compound **6o** *anti*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–6.70 (m, 8H), 5.04 (d, J=9.4 Hz, 1H), 4.80 (dd, J=17.6, 3.2 Hz, 1H), 4.62 (dd, J=50.2, 3.1 Hz, 1H), 3.76 (s, 3H), 3.62 (dd, J=24.9, 9.5 Hz, 1H).• ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (d, J=262 Hz), 158.8, 139.9, 133.4, 129.5, 129.5, 128.9 (d, J=2 Hz), 128.2 (2C), 128.1 (2C), 113.9 (2C), 93.0 (d, J=20 Hz), 74.4 (d, J=3 Hz), 56.8 (d, J=24 Hz), 55.1. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.9 (ddd, J=50, 25, 18 Hz). Compound **6o** *syn*: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–6.68 (m, 8H), 5.16 (d, J=8.1 Hz, 1H), 4.48 (dd, J=18.0, 3.1 Hz, 1H), 4.23 (dd, J=50.4, 3.1 Hz, 1H), 3.83 (s, 3H), 3.59 (dd, J=22.7, 9.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 (d, J=260 Hz), 159.3, 140.1, 133.6, 130.0, 129.9, 128.5, 128.4 (2C), 127.9 (2C), 114.3 (2C), 92.8 (d, J=21 Hz), 73.8, 56.9 (d, J=24 Hz), 55.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ −101.3 (ddd, J=50, 23, 18 Hz). IR (cm^{-1}): 3463, 2837, 1669, 1610, 1510, 1245, 1177, 1031, 1012. Anal. Calcd for $C_{17}H_{16}ClFO_2$: C, 66.65; H, 5.26. Found: C, 66.25; H, 5.48.

Acknowledgements

This work has been partially supported by INSA Rouen, Rouen University, CNRS, EFRD, Labex SynOrg (ANR-11-LABX-0029) and Région Haute-Normandie (CRUNCh network). G.L. and N.V.H. thank the EFRD for a postdoctoral fellowship (EFRD 32819 & EFRD 43209).

References and notes

1. (a) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308–319; (b) Bégué, J.-P.; Bonnet-Delpon, D. *Bioorganic and Medicinal Chemistry of Fluorine*; John Wiley & Sons: Hoboken, NJ, 2008; (c) Kirsch, P. *Modern Fluoorganic Chemistry*; Wiley-VCH: Weinheim, Germany, 2004; (d) Mikami, K.; Itoh, Y.; Yamanaka, M. *Chem. Rev.* **2004**, *104*, 1–16.
2. (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881–1886; (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320–330.
3. For review on fluorine introduction see: (a) Furuya, T.; Kuttruff, C. A.; Ritter, T. *Curr. Opin. Drug. Discovery Dev.* **2008**, *11*, 803–819; (b) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470–477; (c) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8214–8264; (d) Hollingworth, C.; Gouverneur, V. *Chem. Commun.* **2012**, 2929–2942.
4. (a) Landelle, G.; Bergeron, M.; Turcotte-Savard, M.-O.; Paquin, J.-F. *Chem. Soc. Rev.* **2011**, *40*, 2867–2908; (b) Yanai, H.; Taguchi, T. *Eur. J. Org. Chem.* **2011**, 5939–5954; (c) Hara, S. *Top. Curr. Chem.* **2012**, *327*, 59–86 For selected examples regarding the fluoroalkenes synthesis, see: (d) Yang, M.-H.; Matikonda, S. S.; Altman, R. A. *Org. Lett.* **2013**, *15*, 3894–3897; (e) Cao, C.-R.; Ou, S.; Jiang, M.; Liu, J.-T. *Org. Biomol. Chem.* **2014**, *12*, 467–473.
5. Selected examples: (a) Dutheuil, G.; Couve-Bonnaire, S.; Pannecoucke, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 1290–1292; (b) Pierry, C.; Couve-Bonnaire, S.; Guilhaudis, L.; Neveu, C.; Marotte, A.; Lefranc, B.; Cahard, D.; Ségalas-Milazzo, I.; Leprince, J.; Pannecoucke, X. *ChemBioChem* **2013**, *14*, 1620–1633; (c) Van der Veken, P.; Senten, K.; Kertèsz, I.; De Meester, I.; Lambeir, A.-M.; Maes, M.-B.; Scharpé, S.; Haemers, A.; Augustyns, K. *J. Med. Chem.* **2005**, *48*, 1768–1780; (d) Zhao, K.; Lim, D. S.; Funaki, T.; Welch, J. T. *Bioorg. Med. Chem.* **2003**, *11*, 207–215 For reviews see: (e) Couve-Bonnaire, S.; Cahard, D.; Pannecoucke, X. *Org. Biomol. Chem.* **2007**, *5*, 1151–1157; (f) Taguchi, T.; Yanai, H. In *Fluor. Med. Chem. Chem. Biology*; Ojima, I., Ed.; Blackwell: 2009; p 257.
6. (a) Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Chem. Commun.* **2007**, 1003–1022; (b) Babudri, F.; Cardone, A.; Farinola, G. M.; Martinelli, C.; Mendichi, R.; Naso, F.; Striccoli, M. *Eur. J. Org. Chem.* **2008**, 1977–1982.
7. Deng, T.; Shan, S.; Li, Z.-B.; Wu, Z.-W.; Liao, C.-Z.; Ko, B.; Lu, X.-P.; Cheng, J.; Ning, Z.-Q. *Biol. Pharm. Bull.* **2005**, *28*, 1192–1196.
8. Oishi, S.; Kamitani, H.; Kodera, Y.; Watanabe, K.; Kobayashi, K.; Narumi, T.; Tomita, K.; Ohno, H.; Naito, T.; Kodama, E.; Matsuoka, M.; Fujii, N. *Org. Biomol. Chem.* **2009**, *7*, 2872–2877.
9. Selected examples: (a) Makita, N.; Hoshino, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 941–9434; (b) Blanc, A.; Toste, F. D. *Angew. Chem., Int. Ed.* **2006**, *45*, 2096–2099; (c) Malkov, A. V.; Barlóg, M.; Miller-Potucká; Kabeshov, L. M. A.; Farrugia, L. J.; Kocovsky, P. *Chem.—Eur. J.* **2012**, *18*, 6873–6884.
10. (a) Poisson, T.; Belhomme, M.-C.; Pannecoucke, X. *J. Org. Chem.* **2012**, *77*, 9277–9285; (b) Ivashkin, P.; Couve-Bonnaire, S.; Jubault, P.; Pannecoucke, X. *Org. Lett.* **2012**, *14*, 5130–5133; (c) Milanole, G.; Couve-Bonnaire, S.; Bonfanti, J.-F.; Jubault, P.; Pannecoucke, X. *J. Org. Chem.* **2013**, *78*, 212–223; (d) Lemonnier, G.; Zoute, L.; Quirion, J.-C.; Jubault, P. *Org. Lett.* **2010**, *12*, 844–846; (e) Belhomme, M.-C.; Poisson, T.; Pannecoucke, X. *Org. Lett.* **2013**, *15*, 3428–3431; (f) David, E.; Milanole, G.; Ivashkin, P.; Couve-Bonnaire, S.; Jubault, P.; Pannecoucke, X. *Chem.—Eur. J.* **2012**, *18*, 14904–14917; (g) Colombel, S.; Van Hijfte, N.; Poisson, T.; Leclerc, E.; Pannecoucke, X. *Chem.—Eur. J.* **2013**, *19*, 12778–12787.
11. Allmendinger, T.; Angst, C.; Karfunkel, H. *J. Fluorine Chem.* **1995**, *72*, 247–253.

12. Hassan, A.; Montgomery, T. P.; Krische, M. J. *Chem. Commun.* **2012**, 4692–4694.
13. Hayashi, T.; Usuki, Y.; Iio, H. *J. Fluorine Chem.* **2010**, *131*, 709–713.
14. For reviews dealing with the use of indium (0) in allylation reaction see: (a) Bowyer, W. J.; Singaram, B.; Sessler, A. M. *Tetrahedron* **2011**, *67*, 7449–7460; (b) Augé, J.; Lubin-Germain, N.; Uziel, J. *Synthesis* **2007**, 1739–1764; (c) Shen, Z.-L.; Wang, S.-Y.; Chok, Y.-K.; Xu, Y.-H.; Loh, T.-P. *Chem. Rev.* **2013**, *113*, 271–401.
15. For a preliminary communication from our group, see: Lemonnier, G.; Poisson, T.; Couve-Bonnaire, S.; Pannecoucke, X. *Tetrahedron Lett.* **2013**, *54*, 2821–2824.
16. For a beneficial effect of brine or saturated aqueous solution in indium promoted allylation reaction see: Sun, X.-W.; Liu, M.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2008**, *10*, 1259–1262.
17. So far, we have not been able to determine the stereochemistry of the product.
18. Lemonnier, G.; Zoute, L.; Dupas, G.; Quirion, J.-C.; Jubault, P. *J. Org. Chem.* **2009**, *74*, 4124–4131.
19. For examples of γ-selectivity with In see: (a) Ranu, B. C.; Samanta, S.; Hajra, A. *J. Org. Chem.* **2001**, *66*, 7519–7521; (b) Cha, J. H.; Pae, A. N.; Choi, K. I. I.; Cho, Y. S.; Koh, H. Y.; Lee, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2079–2081; (c) Cho, Y. S.; Kang, K. H.; Cha, J. H.; Choi, K. I.; Pae, A. N.; Koh, H. Y.; Chang, M. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 1285–1290; (d) Hirashita, T.; Inoue, S.; Yamamura, H.; Kawai, M.; Araki, S. *J. Organomet. Chem.* **1997**, *549*, 305–309; (e) Woo, S.; Squires, N.; Fallis, A. G. *Org. Lett.* **1999**, *1*, 573–575.
20. The X-ray structure has been deposited (*anti*-**6a** CCDC 951873) at the Cambridge Crystallographic Data Center.
21. Similar isomerisation have been previously proposed: (a) Paquette, L. A.; Mitzel, T. M. *J. Org. Chem.* **1996**, *61*, 8799–8804; (b) Isaac, M. B.; Chan, T.-H. *Tetrahedron Lett.* **1995**, *36*, 8957–8960; (c) Ho, D. S.-C.; Sim, K.-Y.; Loh, T.-P. *Synlett* **1996**, 263–264.